Unusual Field-Coupled Nonlinear Continuum Mechanics of Smart Materials

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Abstract

A set of anisotropic constitutive relations are developed using nonlinear continuum mechanics to model chemical and field-coupled material behavior in a relatively broad range of smart materials. A Landau-based free energy function is formulated and numerically implemented to elucidate how finite deformation and crystal anisotropy affect field-coupled deformation and how deformation affects microstructure evolution. Rotationally invariant order parameters are introduced within the Landau energy function to illustrate how field-coupled mechanics occurs without introducing explicit phenomenological parameters. Spontaneous deformation due to scalar, vector, and tensor order parameters is quantified using this approach. It is shown that both the scalar and vector order parameters induce hydrostatic deformation while the second order tensor order parameter induces a range of different anisotropic spontaneous deformation states. Numerical simulations are given which illustrate unusual field-coupled microstructure evolution for a select number of active materials in comparison with data given in the literature. The materials simulated range from chemically responsive glassy polymer networks,

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soft polydomain liquid crystal elastomers, and tetragonal phase ferroelectric materials. The results illustrate that finite deformation continuum mechanics can be useful in modeling many unusual field-coupled, anisotropic constitutive relations without introducing explicit coupling parameters.

1 Introduction

Smart materials are well known for their intrinsic field coupled material characteristics which in many cases can provide simultaneous actuation and sensing for adaptive structure applications. This unique multifunctionality has been the impetus for studying field-coupled mechanics for several decades. Arguably, the most well known types of smart materials include ferroelectric ceramics (Lines and Glass, 1977; Jaffe et al., 1971), magnetostrictive compounds (Bertotti, 1998; Kittel, 1949), and shape memory alloys (Boyd and Lagoudas, 1996; Huang and Brinson, 1998). Active polymers have also begun to emerge as viable artificial muscles (Bar-Cohen and Zhang, 2008). These materials include dielectric elastomers (Kofod and Sommer-Larsen, 2005), shape memory polymers (Lendlein and Kelch, 2002), ionic polymers (Nemat-Nasser, 2002), and a relatively broad class of nanocomposites (Baur and Silverman, 2007) and liquid crystal elastomers (Warner and Terentjev, 2007).

A broad range of constitutive modeling frameworks have been developed to predict the material behavior governing active materials. For a review of continuum methods applied to active materials such as ferroelectric materials, magnetostrictive compounds, and shape memory alloys, see (Smith, 2005; Bertotti, 1998; Boyd and Lagoudas, 1996; Huang and Brinson, 1998; Seelecke and Müller, 2004; Huang and Brinson, 1998; J.E.Huber et al., 1999; J.E.Huber and N.A.Fleck, 2001; Hwang and Arlt, 2000; Armstrong, 2000; Kamlah et al., 2008) and many others. Efforts have also focused on extracting underlying material relations via configurational forces or multiscale mechanics to understand how local defects may influence micro to mesoscale behavior (Hildebrand and Abeyaratne, 2008; Kowalewsky, 2004; Su and Landis, 2007). Model development specific to liquid crystal elastomers can be found in (Warner and
Unified theories have also been developed with particular emphasis on fundamental electromagneto-elastics of solids which includes extensive analysis of the fundamental balance laws and generalized constitutive relations (Maugin, 2011; Ericksen, 2008; Vu and Steinmann, 2010; Toupin, 1963; Nelson, 1991; Hutter and Van, 1978; Trimarco, 2009). However, specific free energy functions and the corresponding constitutive relations that correlate polarization, magnetization, liquid crystal order, phase and deformation with experiments still present significant challenges. One example of a unified constitutive model for ferroic materials (i.e., ferroelectric, ferromagnetic, shape memory alloy) has been developed which includes nonlinear and hysteretic rate-dependent material behavior for small strain problems under uniaxial loading (Smith et al., 2006; Smith, 2005). A combination of continuum thermodynamics and statistical mechanics was used to develop a homogenized energy model to predict the field-coupled constitutive behavior.

Finite deformation electro-mechanics and magneto-mechanics modeling has also been studied in soft elastomeric materials (Zhao et al., 2007; Suo et al., 2008; McMeeking and Landis, 2005; Bustamante et al., 2008, 2009). For dielectric elastomers, it was shown that a superposition of a mechanical energy function and an idealized dielectric energy function leads to coupling between deformation of a polymer network and electrostatic fields. A set of electrostatic stresses were obtained based on fundamental thermodynamics and nonlinear continuum mechanics. Whereas this concept has been shown to provide good predictions of electrostatic stresses in dielectric elastomers, limited work has been conducted to correlate anisotropic microstructure evolution in a broader class of active materials using nonlinear continuum mechanics.

The concept of a microforce has been explored to quantify underlying microstructure evolution in solids with emphasis on quantifying solid-solid phase evolution (Fried and Gurtin, 1994; Gurtin, 1996). This approach involves modeling an order parameter and its gradient in combination with linear momentum to correlate the constitutive behavior during phase transformations and microstructure evolution. The minimization of the free energy of the
order parameter results in an Euler-Lagrange equation that has been used extensively in modeling a wide range of meso to microscale effects in active materials (Cao and Cross, 1991; Virga, 1994; Kittel, 1949; Chen, 2002). Whereas finite deformation was included in the microforce balance that was described in (Gurtin, 1996), limited model development has been conducted to correlate energy functions and constitutive relations for field-coupled and chemically-coupled materials.

In this analysis, nonlinear mechanics is coupled with microstructure evolution and numerically implemented to quantify coupling between different order parameters (e.g., polarization, liquid crystal order, and water vapor concentration) based on finite deformation mechanics. These different order parameters range from scalar, vector, and second order tensors which are used to compare the modeling framework with experimental results given in the literature. It is shown that the superposition of mechanical energy and a multi-well free energy that describes the underlying microstructure is sufficient to predict many field-coupled constitutive relations without introducing explicit phenomenological coupling parameters. Moreover, the methodology is used to illustrate that this coupling remains in the limit of infinitesimal strain as described by a comparison to experiments on ferroelectric materials. This is done by fitting the dielectric and elastic constants and predicting piezoelectric coupling in ferroelectric lead zirconate titanate. Recently unusual piezoelectricity was measured using time-resolved x-ray experiments (Jones et al., 2007; Pramanick et al., 2011). A tensor order parameter is proposed to predict this behavior instead of the typical polarization order parameter.

The free energy function includes a chemical potential governing the phase, anisotropy energy for long range crystal anisotropy in a three dimensional solid, and an isotropic energy for lower order nematic phase that occurs in liquid crystal polymer networks. This leads to predictions of anisotropic deformation or swelling that is driven by the underlying microstructure and chemical changes. A relatively small number of material parameters (six or less) is able to predict the salient features governing anisotropic, field-coupled or chemically-coupled deformation. Conversely, applied traction on the surface or applied fields also lead to deformation and changes in the internal microstructure. Predictions of bending deformation of
chemically responsive elastomers, unusual soft elasticity of polydomain nematic phase liquid crystal elastomers, and anisotropic piezoelectricity and polarization switching of ferroelectric materials are simulated to illustrate how the model can be used to predict a relatively broad range of field-coupled material characteristics. In particular, experimental results given in the literature are used as motivation for comparisons to the model (Harris et al., 2005; Urayama et al., 2009; Jones et al., 2007; Pramanick et al., 2011).

In the following sections, a general set of governing equations are briefly described and followed by numerical examples. In Sections 2 and 3, a brief review of the balance equations and thermodynamic relations are given. In Section 4, several numerical results describing how the model is applicable to a relatively broad number of active materials are presented. Discussion and concluding remarks are given in the final two sections.

2 Governing Equations

The model is first considered by starting with a free energy description per current volume

\[ \psi = \psi_M(F_{IK}) + \psi_A(c, c_i, \phi_i, \phi_{i,j}, Q_{ij}, Q_{ij,k}) \]  

where the energy is decomposed into mechanical effects in \( \psi_M \) and active microstructure effects in \( \psi_A \). The order parameters range from scalar, vector, and tensor order parameters that are defined in the spatial configuration. The scalar order parameter \( c \) and its gradient \( c_{,i} \), are used to quantify chemically induced deformation as a function of changes in concentration. The vector order parameter, \( \phi_i = \{P_i, M_i, n_i\} \), may include polarization \( P_i \), magnetization \( M_i \), or liquid crystal order \( n_i \), for example. The gradient on the order parameter is denoted by \( \phi_{i,j} \) and is often included in meso to microscale energy descriptions to approximate a multipole expansion on electrostatic or magnetostatic behavior that gives rise to twinned domain structures within a grain or single crystal material (Lines and Glass, 1977; Mitsui and Furuichi, 1953). A tensor order parameter and its gradient has also been introduced as \( Q_{ij} \) and \( Q_{ij,k} \); respectively. This tensor is normally used to quantify quadrupole effects. Such
effects are normally negligible in materials with strong polarization or magnetization, but the quadrupole tensor is typically the primary order parameter used in modeling a class of active materials called liquid crystal polymer networks (LCNs) (Warner and Terentjev, 2007; P. de Gennes and Prost, 1993). Tensor order parameters have also been used to model a strain-like order parameter in ferromagnetic shape memory alloys to accommodate relatively large strain changes near twinned martensitic variants that otherwise exhibit significantly large stress concentrations (Landis, 2008).

When modeling liquid crystal polymer networks, the second order tensor order parameter is related to the vector order parameter or director by $Q_{ij} = Q/2(3n_in_j - \delta_{ij})$. In this equation, $Q$ defines the order of the nematic phase and $n_i$ is constrained to a unit vector that defines the orientation of a rod-like liquid crystal cluster of uniformly aligned molecules. This form only includes the deviatoric component such that anisotropic dielectric properties or the light absorption tensor can be defined to be proportional to the tensor order parameter. Different approaches have been proposed to address how to incorporate $Q$ and $n_i$ into a modeling framework; see (Ericksen, 1991) for comparisons. One potential method is to directly model $Q_{ij}$ as the tensor order parameter since it is measurable from nuclear magnetic resonance techniques or indirectly from optical measurements (P. de Gennes and Prost, 1993). Here, we will numerically implement a reduced order method that simulates the director as the vector order parameter using the quadrupole definition, $Q_{ij} = 1/2(3n_in_j - n_0^2\delta_{ij})$ where $n_0$ is the equilibrium director value for a monodomain and $0 \leq |n| \leq 1$ instead of a unit vector. This accommodates both $Q$ and the traditional unit vector representation of the director into a single vector order parameter and allows for the introduction of a relative simple free energy function with a phase field model. However, this can lead to an approximation of $Q_{ij}$ when the model is implemented numerically using phase field methods due to a diffuse domain wall, point or line defect. This is because the trace of $Q_{ij}$ may not be zero in regions of defects. Despite this approximation, it provides a reduced order phase field modeling approach that only requires simulating three vector components versus five tensor components with the constraint $Q_{kk} = 0$. The differences in direct implementation of the quadrupole tensor versus
the director vector order parameter will be discussed in a future analysis.

A number of mechanical energy functions can be introduced to quantify stress-strain constitutive behavior such as an anisotropic elastic constitutive law, or in the case of elastomers, a hyperelastic energy function; see (Holzapfel, 2000) for examples. Here, coupling between a generalized mechanical energy function is first presented. Specific mechanical and order parameter energy functions will be given in subsequent sections to first provide qualitative estimates on spontaneous strain as a function of material parameters and second, more quantitative estimates for different active materials using numerical simulation.

It is initially assumed that these materials can undergo finite deformation without fracture. The assumption of large deformation is used to quantify the material coupling based on nonlinear geometric effects and thermodynamic parameters in the reference configuration, but the model is also shown to exhibit interesting coupling in the limit of infinitesimal strain as will be shown for the case of lead zirconate titanate piezoelectric materials. To this end, the nonlinear continuum model is formulated to include finite deformation which requires introducing the deformation gradient.
\[ F_{iK} = \frac{\partial x_i}{\partial X_K} \]  

where \( x_i \) is the spatial point and \( X_K \) is the reference or material point (Malvern, 1969).

A set of relations are introduced to provide rotational invariance in the reference configuration. The scalar, vector, and tensor order parameter relations in the reference and current configuration are related by

\[
\begin{align*}
\phi_i &= J^{-1} F_{iK} \tilde{\phi}_K \\
\phi_{ij} &= J^{-1} F_{iK} F_{jL} \tilde{\phi}_{K,L} \\
Q_{ij} &= J^{-1} F_{iK} F_{jL} \tilde{Q}_{KL} \\
c &= J^{-1} \tilde{c} \\
c_{,i} &= J^{-1} F_{iK} \tilde{c}_{,K}
\end{align*}
\]

(3)

where the tilde (\( \tilde{\cdot} \)) denotes order parameters in the reference configuration. The Jacobian is defined by \( J = \text{det}(F_{iK}) \). The relations (3)\(_{1,4}\) can be obtained using geometric arguments and conservation of mass, respectively (Malvern, 1969). The remaining terms can be determined using the principle of virtual work by introducing work conjugate variables for the order parameter and its gradient; see (Zhao et al., 2007; Oates and Wang, 2009) for examples on dielectric elastomers and liquid crystal elastomers. A similar relation can be introduced for the second order tensor gradient, although we will focus on the reduced order approach that relates the gradient of \( Q_{ij} \) to the gradient of the vector order parameter in this analysis. It should be noted that this is not the only form that satisfies rotational invariance. The rotation tensor could also satisfy invariance; however, determination of the field-coupled stresses is more complex; see (McMeeking and Landis, 2005). The introduction of these relations will be introduced into (1) to quantify material coupling based on nonlinear geometric effects.

Minimization of the free energy and kinetic energy per reference volume requires satisfying linear momentum and microscale force balances on the order parameters \( \tilde{\phi}_I \) and \( \tilde{c} \). Note that in the present analysis \( \tilde{Q}_{KL} \) is defined to depend on the vector order parameter, so a tensor-based
Euler-Lagrange equation is not introduced for this tensor. These equations are

\[
\frac{\partial s_{iK}}{\partial X_K} + B_i = 0
\]

\[
\frac{\partial \tilde{\xi}_{JI}}{\partial X_J} + \tilde{\pi}_I + \tilde{\gamma}_I = 0
\]

\[
\frac{\partial \tilde{\nu}_J}{\partial X_J} + \tilde{\nu} + \tilde{\gamma} = 0
\]

in the reference volume \( \Omega_0 \) where the first equation is the quasi-static form of linear momentum, the second equation describes a microforce balance on the vector order parameter \( \tilde{\phi}_I \) and the third equation describes a chemical potential balance. The nominal stress is defined by \( s_{iK} \) and the body force is denoted by \( B_i \). The microforce balance is governed by the micro-stress tensor \( \tilde{\xi}_{JI} \), an internal body force \( \tilde{\pi}_I \), and an external body force \( \tilde{\gamma}_I \). This form of the governing equations is useful in formulating a computational framework in the reference configuration. More details on the microforce and chemical potential balance equations can be found in (Gurtin, 1996). Additional details that define these work conjugate variables in terms of the free energy function are given in the following section.

A set of boundary conditions are defined for (4)\(_{1,2}\). For linear momentum, traction is defined by \( T_i = s_{iK} \hat{N}_K \) on \( \Gamma_0 \). The unit normal in the reference description is denoted by \( \hat{N}_K \). The boundary conditions for the microforce balance include \( \tilde{\tau}_I = \tilde{\xi}_{JI} \hat{N}_J \) on \( \Gamma_0 \).

The chemical flux relations on the surface and within the volume require coupling (4)\(_3\) with the conservation of mass

\[
\dot{\tilde{c}} = -\tilde{J}_{I,J} + \dot{\tilde{m}} \quad \text{in} \quad \Omega_0
\]

where \( \tilde{J}_I \) is the mass flux and \( \dot{\tilde{m}} \) is the external mass density supply rate. The mass flux is assumed to be proportional to the gradient of the chemical potential

\[
\tilde{J}_I = -A_{I,J} \tilde{\mu}_{,J}
\]

where \( \tilde{\mu} \) is the chemical potential and \( A_{I,J} \) is a mobility tensor.
Phase evolution is often described by combining the conservation of mass and the chemical potential balance relations which leads to the Cahn-Hilliard equation (J. Cahn, 1961). This is obtained by solving (4) as \( \bar{\pi} = -\tilde{\xi}_{K,K} - \tilde{\gamma} \) and writing the work conjugate relation for the chemical potential as \( \bar{\mu} = \frac{\partial \tilde{\psi}}{\partial \bar{c}} + \tilde{\pi} \), as discussed in detail in (Gurtin, 1996; Govindjee and Simo, 1993). Substituting these relations together with (6) into (5) gives the Cahn-Hilliard equation

\[
\dot{\bar{c}} = \left( A_{IJ} \left( \frac{\partial \tilde{\psi}}{\partial \bar{c}} - \tilde{\gamma} - \tilde{\xi}_{K,K} \right) \right)_{J,I} + \dot{m}.
\]

(7)

Numerically, this equation is more easily solved in the original form that contains two second order equations that describe conservation of mass (5) and the chemical potential balance (4).

A dissipative force based on the time derivative of \( \tilde{\phi}_I \) will be introduced within the definition of \( \tilde{\pi}_I \). To satisfy objective rates on this vector order parameter, the time derivative of (3) is taken. This leads to an objective rate governed by

\[
\dot{\tilde{\phi}}_K = J H_{iK} \dot{\phi}_i
\]

(8)

where \( \dot{\tilde{\phi}} = \dot{\phi} - \nabla \cdot v \tilde{\phi} + F^{-1} L F \tilde{\phi} \). This objective rate includes the divergence of velocity \( \nabla \cdot v \) for compressible deformation processes (i.e., \( \dot{J} \neq 0 \)) and the velocity gradient which is defined by \( L_{ij} = \frac{\partial v_i}{\partial x_j} \) (Malvern, 1969). This form of the objective rate is similar to a convective time derivative often used in electrodynamic problems (Eringen and Maugin, 1990; Hutter and Van, 1978). The relation described by (8) is used in formulating the dissipative energy relation. This dissipative energy relation is implemented in (4) within the term defined by \( \tilde{\pi}_I \) as a function of the evolution rate of the vector order parameter \( \tilde{\phi}_I \). The dissipative energy is defined as \( \tilde{\Pi}_D = -\frac{\beta_{IJ} \dot{\tilde{\phi}}_I \dot{\tilde{\phi}}_J}{2} \) where \( \beta_{IJ} \) is an inverse mobility tensor.

By taking the variation of the dissipative energy \( \tilde{\Pi}_D \), the microscale body force \( \tilde{\pi}_I \) will include dissipative effects according to

\[
\tilde{\pi}_I = -\tilde{\eta}_I - \beta_{IJ} \dot{\tilde{\phi}}_J
\]

(9)
where a conservative force, $\eta_I$, has been included and will be defined by a thermodynamic potential function in the following section. The second term defines the dissipative effect in terms of the objective microstructure rate and inverse mobility tensor.

Prior to defining the set of work conjugate relations, it is illustrative to first present the nominal stress that is typically defined by $s_{iK} = \frac{\partial \tilde{\psi}}{\partial F_{iK}}$ at equilibrium (Holzapfel, 2000). This free energy is defined in the reference frame based on (1), (3), and $\tilde{\psi} = J\psi$ as

$$s_{iK} = \frac{\partial \tilde{\psi}_M}{\partial F_{iK}} + \frac{\partial \tilde{\psi}_A}{\partial F_{iK}}$$

(10)

which defines the total nominal stress where the first term represents stresses from stretching mechanical bonds and the second term represents stresses from the order parameters. In this formulation, the total nominal stress is based on an objective free energy function which leads to a symmetric, total Cauchy stress. It should also be emphasized that only the total stress is measurable; however, several free energy components are introduced to quantify different internal field-coupled effects.

Also note that the stress in (10) is defined at equilibrium. Additional stresses from rate dependence may occur due to deformation gradient coupling contained within $\tilde{\phi}_I$. In the subsequent numerical simulations, quasi-static loading is considered which will neglect the rate dependent term. The magnitude of this stress component was verified to be negligible for the stretch rates considered on liquid crystal elastomers and ferroelectric microstructure problems for the given inverse mobility coefficients.

In summary, the nominal stress relation forms the key result of the model which illustrates how an order parameter (i.e., polarization, magnetization, liquid crystal order, or changes in concentration) may influence the constitutive behavior of an active material. Special forms of $\tilde{\psi}$ will be given to illustrate how the model predicts anisotropic active material behavior for a select number of active materials. First, a brief description of the thermodynamic relations and work conjugate variables is given.
2.1 Work Conjugate Relations

According to the first and second laws of thermodynamics, the applied power must be equal to or surpass the sum of kinetic energy and free energy rate of the material. By combining the first and second laws and applying the result to an arbitrary representative volume element in the deformed configuration, the balance of work rate to the internally stored free energy rate is

\[
\dot{\rho} \dot{\psi} \leq \sigma_{ji} v_{i,j} + \xi_{ji} \dot{\phi}_{i,j} - \pi_i \dot{\phi}_i + \xi_i \dot{\rho}_i + (\bar{\mu} - \bar{\pi}) \dot{\rho} - J_i \mu_i
\]

where the free energy rate per mass is \(\dot{\psi}\); see (Gurtin, 1996; McMeeking and Landis, 2005) for details. Here, the total Cauchy stress has been introduced as \(\sigma_{ji}\).

The time rate of change of the deformation gradient, \(\frac{dF_{iK}}{dt} = \frac{\partial v_i}{\partial x_j} \frac{\partial x_j}{\partial X_K} = F_{jK} \frac{\partial v_i}{\partial x_j}\), is used to compare the time rate of change of the free energy in (11) using the relation

\[
\dot{\psi} = \frac{\partial \tilde{\psi}}{\partial F_{iK}} \dot{F}_{iK} + \frac{\partial \tilde{\psi}}{\partial \phi_i} \dot{\phi}_i + \frac{\partial \tilde{\psi}}{\partial \phi_{i,j}} \dot{\phi}_{i,j} + \frac{\partial \tilde{\psi}}{\partial \rho_i} \dot{\rho}_i + \frac{\partial \tilde{\psi}}{\partial \rho} \dot{\rho}.
\]

The work conjugate variables are defined by comparing (11) and (12). The free energy is written in terms of energy per volume in terms of the reference density, \(\tilde{\psi} = \tilde{\rho} \tilde{\psi}\) (Holzapfel, 2000). This provides a definition of the total Cauchy stress

\[
\sigma_{ji} = J^{-1} F_{jK} \frac{\partial \tilde{\psi}}{\partial F_{iK}}
\]

where \(J^{-1} = \frac{\rho}{\tilde{\rho}}\). Note that the free energy is assumed to include the effect of mechanics, the order parameters, and electromagnetic energy in free space. Details regarding the form of the objective thermodynamic energy functions for \(\tilde{\psi}\) are introduced in the following section.

The work conjugate body forces and microstresses associated with the vector order parameter are

\[
\eta_i = J^{-1} \frac{\partial \tilde{\psi}}{\partial \phi_i} \quad \text{and} \quad \xi_{ji} = J^{-1} \frac{\partial \tilde{\psi}}{\partial \phi_{i,j}}.
\]
Based on the definition of $Q_{ij}$ in terms of $\phi_i$, the work conjugate field is $\eta_i = J^{-1} \frac{\partial \tilde{\psi}}{\partial Q_{kl}} \frac{\partial Q_{kl}}{\partial \phi_i}$.

It should be noted that only the conservative force that is associated with the first term in (9) is included in the definition of $\eta_i$.

The work conjugate variables associated with the phase are

$$\mu - \pi = J^{-1} \frac{\partial \tilde{\psi}}{\partial c}, \quad \text{and} \quad \xi_i = J^{-1} \frac{\partial \tilde{\psi}}{\partial c, i}.$$  (15)

A substitution of the conjugate variables given in this section plus the spatial form of the relations (9) and (6), into (12) gives

$$\beta_{ij} \dot{\phi}_i \dot{\phi}_j + A_{ij} \mu_{,i} \mu_{,j} \geq 0.$$  (16)

Since $\phi_i$ and $\mu$ are independent variables, both $\beta_{ij}$ and $A_{ij}$ must be positive semi-definite to satisfy the second law of thermodynamics.

### 3 Thermodynamic Energy Functions

The form of the thermodynamic potential used to predict active material coupling and microstructure evolution is presented in this section. An emphasis is placed on simplified free energy functions with a minimal number of parameters necessary to predict a relatively broad range of active material constitutive relations. Whereas additional coupling terms are valid to consider within a free energy formulation, we propose that coupling from rotational invariant order parameters based on a spatial description of the free energy is sufficient to predict a broad range of smart material constitutive relations. Moreover, the utilization of a spatial form of the free energy may reduce the number of phenomenological constants necessary to fit to data as will be illustrated through numerical simulation.

A description of the chemical free energy function is first given followed by the vector and tensor order parameters. The coupled stresses from each energy function are determined and material parameter dependence on spontaneous strain is quantified for the vector and tensor order parameters. Numerical implementation is then given in Section 4.
3.1 Scalar Order Parameter

A chemical free energy is written as a function of the concentration to quantify changes in chemically induced deformation using the relation

$$\psi_c(c) = \frac{g}{2}(c - c_0)^2 + \frac{h}{4}(c - c_0)^4$$

per current volume where a reference concentration has been defined by $c_0$ at some initial time. The phenomenological parameters include $g$ and $h$ which define the magnitude of the chemical potential for a given change in concentration.

Nonlinear coupling between the deformation gradient and the concentration is introduced within this energy function using the relation previously defined by (3). This requires that the free energy in the reference frame be coupled to the deformation gradient via the Jacobian $J$ as described by

$$\tilde{\psi}_c = \frac{gJ}{2}(J^{-1}\tilde{c} - c_0)^2 + \frac{hJ}{4}(J^{-1}\tilde{c} - c_0)^4.$$  \hspace{1cm} (18)

The stress associated with the change in concentration is obtained from $

s_{iK}^c = \frac{\partial \tilde{\psi}_c}{\partial F_{iK}}$

which gives

$$s_{iK}^c = -\frac{g}{2}J^{-1}H_{iK}(\tilde{c}^2 - J^2c_0^2) +$$

$$-\frac{h}{4}H_{iK}(-3J^{-3}\tilde{c}^4 + 8J^{-2}\tilde{c}^3c_0 - 6J^{-1}\tilde{c}^2c_0^2 + Jc_0^4)$$

and the Cauchy stress component associated with chemical diffusion is obtained using the relations (3), (19), and

$$\sigma_{ij}^c = J^{-1}F_{jK} \frac{\partial \tilde{\psi}_A}{\partial F_{iK}}$$

which gives

$$\sigma_{ij}^c = -\left(\frac{g}{2}(c^2 - c_0^2) + \frac{h}{4}(3c^4 - 8c^3c_0 + 6c^2c_0^2 - c_0^4)\right)\delta_{ij}$$  \hspace{1cm} (21)
which leads to hydrostatic stresses relative to the ambient concentration $c_0$. This is expected since absorption of chemical constituents would lead to a volumetric shape change.

### 3.2 Vector Order Parameter

The free energy of the vector order parameter is decomposed into terms that describe three dimensional crystal anisotropy and an isotropic energy function that only governs the magnitude of the order parameter. The anisotropy energy is equivalent to free energy that describes the easy axis in ferromagnetic materials (Kittel, 1949). A similar decomposition has been introduced to study different phases in ferroelectric materials (Heitmann and Rossetti, 2005). While this decomposition is useful to describe crystal anisotropy, it is shown that the rotational invariant vector order parameter plays no role in predicting anisotropic spontaneous deformation.

The three dimensional crystal anisotropy energy focuses on tetragonal phase materials using

$$\psi_{\phi_1} = g|\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl}|\phi_i\phi_j\phi_k\phi_l$$

(22)

where the Kronecker delta is denoted by $\delta_{ij}$. The absolute value of $|\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl}|$ guarantees positive free energy values that are not along the (001) orientation for tetragonal phase crystal symmetry if $g > 0$. This free energy function is plotted in Figure 2(a).

The following isotropic energy function only provides minima that govern the magnitude of the order parameter at equilibrium. It is expanded into an eighth order Landau free function of the form

$$\psi_{\phi_2} = \frac{a_\phi}{2}\phi_i\phi_i + \frac{b_\phi}{4}\phi_i\phi_i\phi_j\phi_j + \frac{c_\phi}{6}\phi_i\phi_i\phi_j\phi_j\phi_k\phi_k + \frac{d_\phi}{8}\phi_i\phi_i\phi_j\phi_j\phi_k\phi_k\phi_l\phi_l$$

(23)

where the phenomenological constants include $a_\phi, b_\phi, c_\phi,$ and $d_\phi$. The effect of each higher order term on spontaneous strain will be quantified in Section 3.4. By substitution of the rotationally invariant order parameter in (3)1 and the relation $\tilde{\psi}_{\phi_2} = J\psi_{\phi_2}$
\[ \tilde{\psi}_{\phi 2} = \frac{a_{ij}^\phi}{2} \tilde{\phi}_i \tilde{\phi}_j + \frac{b_{ijkl}^\phi}{4} \tilde{\phi}_i \tilde{\phi}_j \tilde{\phi}_k \tilde{\phi}_l + \frac{c_{ijklm}^\phi}{6} \tilde{\phi}_i \tilde{\phi}_j \tilde{\phi}_k \tilde{\phi}_l \tilde{\phi}_m \tilde{\phi}_n + \frac{d_{ijklmnop}^\phi}{8} \tilde{\phi}_i \tilde{\phi}_j \tilde{\phi}_k \tilde{\phi}_l \tilde{\phi}_m \tilde{\phi}_n \tilde{\phi}_p \tilde{\phi}_q \]  

(24)

where

\[ a_{ij}^\phi = J^{-1} C_{ij} a_\phi \]
\[ b_{ijkl}^\phi = J^{-3} C_{ijkl} b_\phi \]
\[ c_{ijklm}^\phi = J^{-5} C_{ijklm} C_{mnc_\phi} \]
\[ d_{ijklmnop}^\phi = J^{-7} C_{ijklmnop} C_{pqd_\phi} \]  

(25)

The field coupled stresses associated with this order parameter are determined from the nominal stress definition previously given by (10) and (13). For brevity, only the Cauchy stress is given

\[ \sigma_{ij}^\phi = a_\phi \left( \phi_i \phi_j - \frac{\delta_{ij}}{2} \phi_k \phi_k \right) + b_\phi \left( \phi_i \phi_j - \frac{3\delta_{ij}}{4} \phi_k \phi_k \right) \phi_k \phi_k + \]
\[ c_\phi \left( \phi_i \phi_j - \frac{5\delta_{ij}}{6} \phi_k \phi_k \right) \phi_k \phi_k \phi_l \phi_l + d_\phi \left( \phi_i \phi_j - \frac{7\delta_{ij}}{8} \phi_k \phi_k \right) \phi_k \phi_k \phi_l \phi_l \phi_m \phi_m. \]  

(26)

This symmetric Cauchy stress illustrates order parameter coupling due to the introduction of an objective free energy in (24) and the rotational invariant order parameters in (25). Also note that the crystal anisotropy within \( \psi_{\phi 1} \) does not contribute to the field-coupled stress, as shown in the Appendix. In the case of ferroelectric or ferromagnetic materials where the vector order parameter is polarization or magnetization, the isotropic free energy function is the only direct contributing factor to field-coupled deformation. However, it will be shown in Section 3.4 that this stress is hydrostatic at the equilibrium order parameter value and therefore plays a negligible role in predicting anisotropic deformation exhibited by most types of smart materials.

In the following section, the Cauchy stress due to a second order tensor will be quantified. Comparisons between the vector and tensor order parameter stresses are then given to illustrate deformation predicted by the model under zero stress prior to presenting larger scale
comparative simulations.

3.3 Tensor Order Parameter

The energy function for a tensor order parameter is written in terms of a linear quadrupole that is often used to model liquid crystal materials. While this tensor exist in ferroelectric and ferromagnetic materials, its contribution to the constitutive behavior is normally smaller than the polarization and magnetization (Loudon, 2000). The implications of using this tensor to describe ferroelectric or ferromagnetic materials will be discussed further in Section 5.

The quadrupole free energy function considered here is based on the deviatoric component of a second order tensor. This describes the anisotropic part of a second order tensor such as the dielectric tensor according to $Q_{ij} = \frac{1}{2}(3\kappa_{ij} - \delta_{ij}\kappa_{kk})$ where $\kappa_{ij}$ represents the total dielectric tensor (Ericksen, 1991). The free energy function in terms of $Q_{ij}$ is

$$
\psi_Q = \frac{a_Q}{2} Q_{ij} Q_{ji} + \frac{b_Q}{3} Q_{ij} Q_{jk} Q_{ki} + \frac{c_Q}{4} Q_{ij} Q_{jk} Q_{kl} Q_{li}
$$

(27)

where the phenomenological parameters $a_Q$, $b_Q$, and $c_Q$ govern the order of the crystal structure at the microscopic scale. The functional form of this free energy is identical to the Landau-de-Gennes free energy function used to model liquid crystals (P. de Gennes and Prost, 1993). An example of this free energy is plotted in Figure 2(b) for $a_Q < 0$, $b_Q > 0$, and $c_Q > 0$.

Similar to the vector order parameter free energy, a transformation to the reference domain is introduced to numerically implement the free energy function in the reference configuration for solid mechanics modeling. In the reference frame, the free energy is

$$
\tilde{\psi}_Q = \frac{1}{2} a_Q^{Q}_{ijkl} \tilde{Q}_{ij} \tilde{Q}_{kl} + \frac{1}{3} b_Q^{Q}_{ijklmn} \tilde{Q}_{ij} \tilde{Q}_{kl} \tilde{Q}_{mn} + \frac{1}{4} c_Q^{Q}_{ijklmns} \tilde{Q}_{ij} \tilde{Q}_{kl} \tilde{Q}_{mn} \tilde{Q}_{rs}
$$

(28)

where rotational invariance is satisfied by introducing (3) and $\tilde{\psi}_Q = J\psi_Q$ into (27). These tensors are
\[ a^Q_{ijkl} = J^{-1}C_{IL}C_{JK}Q \]
\[ b^Q_{ijklmn} = J^{-2}C_{IN}C_{JK}C_{LM}b_Q \]
\[ c^Q_{ijklmnrs} = J^{-3}C_{IS}C_{JK}C_{LM}C_{NRC} \]  

(29)

where the Green deformation tensor, \( C_{KL} = F_{iK}F_{iL} \), has been introduced (Malvern, 1969).

For brevity, the nominal stress components are given in the Appendix. The Cauchy stress component induced by the tensor order parameter is determined from (10), (13), and (28) and given by

\[
\sigma^Q_{ij} = a_Q \left( 2Q_{ik}Q_{jk} - \frac{1}{2}Q_{mn}Q_{mn}\delta_{ij} \right) + c_Q \left( 2Q_{ik}Q_{km}Q_{mj} - \frac{2}{3}Q_{kl}Q_{lm}Q_{mk}\delta_{ij} \right) + c_Q \left( 2Q_{ik}Q_{km}Q_{ml}Q_{lj} - \frac{3}{4}Q_{kl}Q_{lm}Q_{mn}Q_{nk}\delta_{ij} \right). 
\]

(30)

It will be shown in the following section that this tensor order parameter can induce either prolate or oblate material behavior meaning positive spontaneous strain may occur in the direction of larger anisotropy (prolate) or negative spontaneous strain in the direction of larger anisotropy (oblate). Furthermore, since the sign of spontaneous strain changes relative to the anisotropy, it is shown in the following section that a certain ratio of the phenomenological

![Figure 2: Free energy plots for the nonlinear continuum model. (a) Anisotropy energy described by \( \psi_{\phi_1} \) in (22). (b) The second order tensor energy function described by \( \psi_Q \) in (27). (c) The combined free energy function \( \psi = \psi_{\phi_1} + \psi_Q \).](a) (b) (c)
parameters decouple spontaneous strain from the tensor order parameter.

### 3.4 Order Parameter Induced Spontaneous Deformation

To illustrate the deformation predictions from the order parameter and free energy relations, an isotropic elastic free energy function is added to the model such that “mechanical” stresses are balanced with the stresses induced by the order parameters. It is clear from (21) that changes in a scalar order parameter only induces hydrostatic stress so this stress is not analyzed here. Instead, comparisons between the vector and tensor order parameter are given to illustrate anisotropic deformation or lack thereof. We will also focus on the small strain limit to simplify the analysis. Detailed numerical analyses, including finite deformation, are given in subsequent sections using elastic and hyperelastic free energy functions and coupling with the order parameters.

The isotropic elastic free energy is denoted by

$$\psi_M = \frac{1}{2} \left( \frac{E}{(1 + \nu)(1 - 2\nu)} \varepsilon_{ii} \varepsilon_{kk} + \frac{E}{1 + \nu} \varepsilon_{ij} \varepsilon_{ij} \right)$$

(31)

where $E$ and $\nu$ are the elastic modulus and Poisson ratio. Infinitesimal strain is denoted by $\varepsilon_{ij}$. The “mechanical” Cauchy stress relation is then given by

$$\sigma_{ij}^M = \frac{E\nu}{(1 + \nu)(1 - 2\nu)} \varepsilon_{kk} \delta_{ij} + \frac{E}{1 + \nu} \varepsilon_{ij}.$$  

(32)

where this stress is added to the field-coupled stress which defines the total Cauchy stress based on the free energy. This total stress is set to zero to quantify spontaneous strain. Anisotropic deformation is computed for a uniformly aligned microstructure vector and tensor order parameter (i.e., monodomain) in the $X_3$ direction. This gives $\phi_3 = \phi_0$ and $\phi_1 = \phi_2 = 0$ for the vector order parameter and $Q_{11} = Q_{22} = -\frac{Q}{2}$ and $Q_{33} = Q$ for the tensor order parameter. In the case of equilibrium under zero applied loads, the total Cauchy stress is zero ($\sigma_{ij} = \sigma_{ij}^M + \sigma_{ij}^A = 0$) where $\sigma_{ij}^A$ is the coupled stress based on either (26) or (30). By solving for the spontaneous strain due to the microstructure coupling, we have
\[ \varepsilon_{11}^0 = \varepsilon_{22}^0 = \frac{1}{E} [(\nu - 1)\sigma_{11}^A + \nu\sigma_{33}^A] \]
\[ \varepsilon_{33}^0 = \frac{1}{E} [2\nu\sigma_{11}^A - \sigma_{33}^A]. \] (33)

To further illustrate this coupling behavior, specific examples are given for the spontaneous strain as a function of the vector and tensor order parameter. The limit of incompressibility (i.e., \( \nu = 0.5 \)) is considered which simplifies the form of the spontaneous strain to illustrate salient features governing the coupling behavior.

For the vector order parameter, we have
\[ \varepsilon_{11}^\phi = \varepsilon_{22}^\phi = \frac{\phi_0^2}{2E} (a_\phi + b_\phi \phi_0^2 + c_\phi \phi_0^4 + d_\phi \phi_0^6) \]
\[ \varepsilon_{33}^\phi = -\frac{\phi_0^2}{E} (a_\phi + b_\phi \phi_0^2 + c_\phi \phi_0^4 + d_\phi \phi_0^6) \] (34)

where these spontaneous strain components are equal at the equilibrium value for \( \phi_0 \). In comparison with the energy function in (23), the polynomial expression in (34) is zero at thermodynamic equilibrium. Therefore the spontaneous strain is always zero for incompressible materials when the root of \( \phi_0 \) is chosen at the global energy minimum. It is interesting to note that when the material is compressible, the spontaneous strain is equal in each direction and therefore does not contribute to any anisotropic deformation. It should be noted that a rigorous proof for all values of the Landau coefficients has not been done.

For the tensor order parameter, we have
\[ \varepsilon_{11}^Q = \varepsilon_{22}^Q = \frac{3Q^2}{8E} [4a_Q + 6b_Q Q + 5c_Q Q^2] \]
\[ \varepsilon_{33}^Q = -\frac{3Q^2}{8E} [4a_Q + 6b_Q Q + 5c_Q Q^2] \] (35)

therefore the function, \( 4a_Q + 6b_Q Q + 5c_Q Q^2 \), is important in quantifying the magnitude and sign of the spontaneous deformation. Moreover, this function is zero for a certain set of constants. This is obtained by solving for the equilibrium vector order parameter by equating the work conjugate variable \( \eta_i \), previously given by (14), to zero. This leads to the solution of the equilibrium microstructure vector order parameter.
\[ Q = \frac{-b_Q \pm \sqrt{b_Q^2 - 4a_Qc_Q}}{2d_Q} \]  

(36)

Normally \( a_Q < 0 \) and \( c_Q > 0 \) for a non-zero, real order parameter value. This relation for \( Q \) is substituted into (35) and the case of zero spontaneous strain is obtained. It can be shown that if

\[ c_Q = -\frac{2b_Q^2}{a_Q} \]  

(37)

the spontaneous deformation is always zero at the equilibrium, positive \( Q \) root for incompressible materials. If \( c_Q < -\frac{2b_Q^2}{a_Q} \) the spontaneous deformation is prolate and if \( c_Q > -\frac{2b_Q^2}{a_Q} \) the spontaneous deformation is oblate. Similar behavior is known to occur in liquid crystal elastomers, however, prolate behavior predominately occurs (Warner and Terentjev, 2007). This decoupling relation will be used in quantifying unusual soft elasticity or lack thereof in polydomain liquid crystal elastomers in Section 4.2. Due to the lack of anisotropic deformation predicted by the vector order parameter, it will also be proposed in Section 4.3 that the tensor order parameter gives a better prediction of electromechanical coupling in ferroelectric materials at the domain length scale.

This form of the free energy function implements a relatively small number of material parameters to explore their effect on predicting complex active material mechanics. Higher order gradients may be necessary to quantify twinned microstructures and interface energetics in materials with heterogeneous microstructure evolution. Whereas finite deformation effects would introduce stresses associated with order parameter gradients, these stresses are typically small due to the magnitude of the phenomenological parameters and are therefore neglected in the numerical simulations.

4 Numerical Implementation

The material model is applied to a select number of active materials that exhibit complex microstructure evolution and nonlinear coupling with deformation. First, deformation from
chemical diffusion is described and compared with data in the literature for large bending deformation of a hygroscopic liquid crystal polymer network (Harris et al., 2005). This is followed by large deformation of a soft polydomain liquid crystal elastomer to show how soft elasticity may or may not occur during uniaxial stretching as a function of the cross-linked reference state. This is motivated by experimental results of polydomain soft elasticity as a function of the cross-linked state (Urayama et al., 2009). Microstructure evolution has shown to be responsible for unusual soft deformation in monodomain specimens, but similar behavior in random polydomains is still not well understood (Biggins et al., 2009). Lastly the model is applied to ferroelectric materials with comparisons to recent unusual anisotropic piezoelectric characterization of lead zirconate titanate (Jones et al., 2007; Pramanick et al., 2011).

### 4.1 Chemically Deforming Materials

The unified model is used to predict large bending deformation induced by water vapor absorption in a hygroscopic liquid crystal polymer network (Harris et al., 2005). This provides an illustration of how volume changes from absorption due to environmental influences affect material deformation. The chemical potential balance, as described by conservation of mass (5) and linear momentum (4) of a finite deforming shell, is used to quantify stress and deformation during changes in concentration. By neglecting localized concentration gradients of multi-phase materials, the chemical potential balance from (4) is neglected and only diffusion of mass and mechanical equilibrium are necessary to predict material deformation from absorption of chemical species from the environment.

The material considered here deforms in the presence of an external water vapor source or pH due to a change in the liquid crystalline structure as the external chemical constituents in the environment are absorbed into the glassy polymer network. The liquid crystal polymer structure initially consists of both covalent and secondary bonds. Humidity-controlled deformation occurs after the network is converted to a salt. This provides a hygroscopic material which begins to swell under humid conditions as water infiltrates the material. The response is relatively fast where reversible deformation can occur on the order of seconds (Harris et al.,
2005). Whereas order-disorder effects of the liquid crystal rod-shaped molecules may also contribute to deformation, the scalar order parameter is able to predict the key deformation characteristics governing these materials.

Prediction of this deformation from water absorption is obtained by implementing the stress coupling with concentration that was described in Section 3.1 into the linear momentum balance equation. Since these materials are typically synthesized as films with thickness on the order of tens of microns, a finite deforming shell model using FEAP is modified to include the chemically induced stress components (Taylor, 2010; Simo and Fox, 1989). Isotropic elastic properties, as a function of the liquid crystal orientation, are introduced based on data given in (Harris et al., 2007). The material parameters used in the constitutive model are given in Table 1. The liquid crystals are aligned along the short axis of the film as denoted by the \( X_1 \) direction which is associated with a larger modulus. The linear chemical potential parameter \( g \) is set to zero in the simulation to illustrate large nonlinear bending deformation. Since \( g \) and \( h \) give different sensitivities to concentration, these parameters can be fit to data based on bending measurements (Hays et al., 2010, 2011). The model model parameter \( h \) was used to qualitatively fit bending simulations to supplemental videos provided in (Harris et al., 2005) where the film rotates approximately 90° as it approaches a water source.

The bending moment is computed by assuming a variation in the relative humidity (RH) in the environment to range between typical ambient conditions of 35% to 100% as the film

Table 1: Water vapor deforming material properties. The orthotropic elastic properties are denoted by the elastic moduli \( E_I \) and Poisson ratio \( \nu_I \). The shear moduli are defined by \( G_I = E_I / (2(\nu_I + 1)) \). The out-of-plane direction is defined as the \( X_3 \) direction.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>( h )</td>
<td>( 1.28 \times 10^{27} ) Nm^9/mol^4</td>
</tr>
<tr>
<td>( E_1 )</td>
<td>2.4 GPa</td>
</tr>
<tr>
<td>( E_2 )</td>
<td>1.6 GPa</td>
</tr>
<tr>
<td>( \nu_1 = \nu_2 )</td>
<td>0.35</td>
</tr>
</tbody>
</table>
approaches a water source. In all simulations, the humidity on the side of the film not exposed to water vapor was held fixed at 35%. The concentration is computed from the ideal gas law and humidity tables assuming ambient temperature (25°C) and atmospheric pressure. This gives a change in water vapor concentration at ambient conditions $c_{0,35\%} = 3.97 \times 10^{-7} \text{ mol/m}^3$ to $c_{100\%} = 1.13 \times 10^{-6} \text{ mol/m}^3$. Using these values for water concentration, a linear increase in concentration is predicted using the boundary value problem for the one dimensional case described in (Bird et al., 1960). For modeling purposes, the ambient conditions are taken far from the water source such that approximately constant concentration is applied to the material surface during large bending deformation.

As the humidity increases to 100%, large chemically induced bending is predicted by computing the “chemically” induced moment using

$$\tilde{m}_{\alpha} = \frac{1}{j} \int_{h^-}^{h^+} \xi \sigma^c \gamma^\alpha j d\xi$$

where $\gamma^\alpha$ is the convected basis which is a function of the deformation gradient and the unit vectors in the reference configuration of the shell model (Simo and Fox, 1989). Note that the initial geometry is considered to be a flat plate. The chemically induced stress is denoted by $\sigma^c$ and is based on (21). Also note that the thickness of the film is $h = h^+ - h^-$ where the coordinate along the thickness direction is $\xi$. The variable $j$ is the mid-surface Jacobian and $(\alpha = 1, 2)$ spans the mid-surface of the shell.

The nonlinear finite element results are illustrated in Figure 3 which include displacement and rotation constraints along the center line of the short axis. The humidity source is located underneath the film. As the humidity is increased from the bottom, the film expands on this surface from water vapor absorption and produces large monotonic increases in bending. Also note that the curvature is largest along the y direction because the modulus is lower in this direction.
4.2 Polydomain Liquid Crystal Elastomers

In comparison to the glassy hygroscopic liquid crystal polymer network, soft elastomers synthesized with liquid crystals are known for their shape change induced by liquid crystal order and conversely, liquid crystal reordering under mechanical loading (Warner and Terentjev, 2007). Due to the soft elastomer network, large liquid crystal reordering may occur during large deformation. Whereas prior work has illustrated microstructure mechanics of these materials in idealized monodomains (Oates and Wang, 2009; Mbanga et al., 2010), it is shown here using the nonlinear continuum model that complex polydomain materials exhibit similar soft elastic behavior (i.e., nonlinear stress-strain response) and transitions from a polydomain to monodomain under large stretch. The effect of the cross-linked reference state is modeled by modifying the Landau coefficients based on the decoupling ratio given by (37).

Since nematic phase liquid crystals do not exhibit three dimensional long range crystal
order, the energy function given by (27) is used to simulate these materials. This corresponds to the free energy plot shown in Figure 2(b). The order parameter for the liquid crystal rod shaped molecule is the director \((n_i = \phi_i)\) which defines a microscale homogenization of the orientation of a mesogen unit. In this case, the second order tensor is defined by

\[
Q^n_{ij} = \frac{1}{2}(3n_in_j - n_0^2\delta_{ij}).
\]

(39)

where the director is limited to the range \(0 \leq |n_i| \leq 1\) by assuming time-averaged thermal fluctuations may reduce the equilibrium director to be \(n_0 \leq 1\). The director at equilibrium is found by setting \(\eta_i = 0\) in (14) which ensures that \(Q_{ij}\) is traceless under zero external loading in regions of a uniform domain.

The experiments given in (Urayama et al., 2009) were conducted by cross-linking the liquid crystal elastomer in either the nematic or isotropic state. It was found that large soft elastic behavior (e.g., nonlinear stress-strain behavior) was observed when the material was cross-linked in the isotropic state, but not the nematic state. When the material is cross-linked in the isotropic state, spontaneous deformation of the host elastomer occurs as nematic phase liquid crystals form during cooling. In the nematic-cross linking state, the nematic phase liquid crystals form prior to formation of the cross-linked elastomer and therefore do not induce spontaneous deformation on the host elastomer network. In this case, we define the reference state to have zero spontaneous deformation for a nematic cross-linked material which requires (37) to hold. For the isotropic cross linked state, \(c_Q < -\frac{2b_Q}{dQ}\) is used to define a prolate liquid crystal elastomer material.

Since polydomain structures are of particular interest, energy penalties on the director gradient are introduced. This energy is described by Frank elastic behavior (P. de Gennes and Prost, 1993). The Frank elastic energy is approximated by a scalar parameter and gradients on the director

\[
\psi_G = \frac{K}{2}n_{i,j}n_{i,j}
\]

(40)

where \(K\) equally penalizes splay, twist, and bend of the liquid crystal director; see (P. de Gennes
and Prost, 1993).

The liquid crystal energy in the spatial domain per current volume is therefore represented by $\psi_A = \psi_Q + \psi_G$. A transformation of the energy to the reference configuration and minimization of the energy leads to an Euler-Lagrange equation of the form

$$\frac{\partial \tilde{\xi}_{IJ}}{\partial X_J} - \tilde{\eta}_I = \beta_0 \tilde{\eta}_I.$$  \hspace{1cm} (41)

This relation is equivalent to (4) except external microforces are neglected. The objective rate $\tilde{\phi}_I = \tilde{\nu}_I$ was defined previously in (8). An inverse mobility factor is defined by $\beta_{IJ} = \beta_0 \delta_{IJ}$ which was also previously defined by the tensor introduced in (9). This mobility factor neglects liquid crystal anisotropy by assuming comparable dissipation in all directions.

The liquid crystal model is coupled to an incompressible hyperelastic neo-Hookean free energy function to predict liquid crystal domain structure evolution. Details of this free energy can be found in (Holzapfel, 2000). The introduction of polymer mechanics requires satisfying linear momentum in the reference configuration as defined by

$$\frac{\partial s_{iK}}{\partial X_K} = 0$$  \hspace{1cm} (42)

where body forces and inertial effects have been neglected. It should be noted that the total nominal stress includes components from the hyperelastic behavior of the host elastomer and the liquid crystal order parameter, $s_{iK} = s^M_{iK} + \frac{\partial \tilde{\psi}_Q}{\partial F_{iK}}$. The first term $s^M_{iK}$ is stress from stretching the elastomer network.

Numerical results are given for a polydomain elastomer that undergoes uniaxial stretching. The equations are implemented numerically using Comsol 3.5 on a quasi-3D domain. A two dimensional problem is simulated using plane stress mechanics but includes the director components in all three directions. Such approximations neglect out-of-plane director gradients and out-of-plane shear coupling with the deformation gradient. The parameters used in the model are based on nominal values for a nematic phase liquid crystal (P. de Gennes and Prost, 1993) and a soft elastomer; see Table 2. The polydomain structure is obtained by using random initial conditions and the model is then allowed to reach equilibrium under zero trac-
Table 2: Parameters used in the finite element model for the isotropic cross-linked case. The parameters include $K$ as the distortional energy constant, $a_Q$, $b_Q$, and $c_Q$ as the Landau parameters, $\mu$ as the shear modulus, and $\kappa$ as the bulk modulus. For the nematic cross-linked state, the parameters were modified as $a_Q = -93.4$ kPa, $b_Q = -96.6$ kPa, $a_Q = \frac{-2b_{Q}^{2}}{c_{Q}} = 200$, and $\mu = 300$ kPa.

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
<th>Unit</th>
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<tr>
<td>$K$</td>
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<td>N</td>
</tr>
<tr>
<td>$a_Q</td>
<td>-1.43</td>
<td>kPa</td>
</tr>
<tr>
<td>$b_Q</td>
<td>-96.6</td>
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<td>$c_Q</td>
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<td>$\beta_0</td>
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<td>N\cdot s/m^2</td>
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<td>GPa</td>
</tr>
<tr>
<td>$\mu</td>
<td>300</td>
<td>kPa</td>
</tr>
</tbody>
</table>

Boundary conditions and roller conditions along the bottom edge. Numerical validation is conducted by using mesh refinement until each computational run gives equivalent results.

Once an equilibrium polydomain configuration is obtained, the model is stretched from the top using a constant velocity, quasi-static displacement control and fully clamped conditions along the bottom.

The results illustrate soft elasticity for the case of $c_Q < -\frac{2b_{Q}^{2}}{a_{Q}}$ and hyperelastic behavior for the decoupled case where $c_Q = -\frac{2b_{Q}^{2}}{a_{Q}}$. Under continued increases in the stretch ratio, the random polydomain elastomer is stretched into an aligned domain structure. In Figure 4, the director component in the vertical direction is plotted at different points along the stress versus stretch curve. Note that the different colors in the plot refer to the director vectors pointing up or down; however, this corresponds to the same energy and strain state. The total nominal stress and stretch is plotted for the stress-stretch components aligned with the load.

During stretching from the initial random state, the volume fraction of domains aligned with the load increases at the expense of domains in other directions. During this process, liquid
crystal reorientation leads to relaxation of the total stress for \( c_Q < -\frac{2b^2}{a_Q} \) (Figure 4(a)) which corresponds to the plateau region. Once all the liquid crystal domain structures align with the external load, the material behaves like a conventional hyperelastic solid. Conversely, when \( c_Q = -\frac{2b^2}{a_Q} \), minimal spontaneous strain occurs at equilibrium prior to stretching. This is not exactly zero everywhere due to defects along domain walls. As the material is stretched, the liquid crystals reorient and align with the external load, but since the spontaneous strain is approximately zero everywhere, no soft elastic plateau is observed. Despite this spontaneous strain decoupling, reorientation of the liquid crystals still occur in the nematic cross-linked model. This is due to the indirect effect of distortion of the Landau-deGennes free energy function in the reference configuration. As the deformation gradient changes, the global energy wells of the free energy function change which leads to driving forces for liquid crystal reorientation.

Similar nonlinear mechanics and increases in the liquid crystal order were observed experimentally in the isotropic and nematic cross-linked state (Urayama et al., 2009). In those experiments, two different cross-link densities (3% and 10%) were tested and similar soft elastic stress-strain curves were measured for isotropic cross-linking and hyperelastic stress-strain curves for nematic cross-linking specimens.

### 4.3 Ferroelectric Materials

Ferroelectric materials are known for their deformation induced by changes in polarization from stress or applied electric fields (Lines and Glass, 1977; Jaffe et al., 1971). This behavior becomes highly nonlinear at large fields and stresses. In this section, the nonlinear continuum modeling framework is applied to tetragonal phase ferroelectric materials to quantify anisotropic, field-induced deformation as a function of four Landau energy parameters and two elastic material parameters without introducing piezoelectric or electrostrictive coefficients.

The choice of the free energy function and order parameters is motivated by time-resolved
Figure 4: Nonlinear deformation of polydomain nematic phase liquid crystal elastomers. The magnitude of the director in the vertical direction is plotted on top of the corresponding stress-strain curves. The bottom edge was fully constrained while stretched at a constant rate of 0.01 µm/s along the top edge. The results in (a) correspond to an isotropic cross-linked state while (b) corresponds to the nematic cross-linked model when $c_Q = -\frac{2b_Q}{a_Q}$.

x-ray data that has shown unusual anisotropic piezoelectric coupling in tetragonal phase lead zirconate titanate materials (Pramanick et al., 2011). In these experiments, large piezoelectric coupling was found when the angle between the applied electric field and polarization was at an angle of approximately $\sim 40^\circ$. The piezoelectricity decreased to approximately zero when the polarization and electric field were parallel or perpendicular. The results suggest polarization rotation and lattice reorientation of the tetragonal crystal structure strongly influences the electro-mechanical behavior. Given this observation, we introduce the second order tensor order parameter to predict anisotropic spontaneous deformation as opposed to the polarization vector order parameter. This is based on the prediction of hydrostatic deformation using a vector order parameter as described in Section 3.4. Comments on this approach versus using explicit coupling between polarization and strain is given in the discussion section.

The tensor order parameter is defined to represent the anisotropic component of the dielec-
electric tensor for tetragonal phase crystal structure. This tensor may be alternatively denoted as a linear quadrupole which introduces additional coupling within Gauss’ law, but is beyond the scope of the present analysis. This behavior will be discussed in a future analysis. Instead, the second order tensor is defined to be proportional to the polarization according to

$$Q_{ij}^P = \frac{1}{2}(3P_iP_j - P_0^2\delta_{ij})$$  \hspace{1cm} (43)

where $P_0$ is the equilibrium value of the polarization and $P_i$ is the polarization in the spatial domain. This gives a set of eigenvectors for $Q_{ij}$ that are orientated parallel or perpendicular to the polarization and is qualitatively consistent with quadrupole calculations based on the effective charge and atom locations using the center of the unit cell as the origin. In the undeformed reference state, the trace of this tensor is zero. This becomes an approximation for large deformation or near twinned domain structures where a direct correlation between $Q_{ij}$ and $P_i$ becomes more difficult. For most ferroelectric crystals, the small strain approximation is reasonable.

The free energy function is constructed by combining the anisotropic energy in (22) with the second order tensor energy function in (27). The combination of these two energy functions given minimima wells for a typical tetragonal phase ferroelectric as illustrated in Figure 2(c). This form of the Landau free energy is combined with the elastic free energy previously given by (31). For numerical implementation, the elastic Cauchy stress tensor in (32) is combined with the second order tensor induced stress given by (30). Note that there is no field-coupled Cauchy stress induced by (22). The Landau parameters, Young’s modulus, and Poisson ratio used in the model for effective monodomain simulations are given in Table 3. Comparisons of these material parameters with a set of parameters for a fully coupled electro-mechanical phase field model are also given. The differences in these models are described in subsequent paragraphs.

Energy minimization at different field increments is first computed to quantify anisotropic piezoelectric behavior and ferroelectric switching behavior for different polarization orientations relative to the applied field. This is obtained through minimization of the electric Gibbs
Table 3: The ferroelectric material parameters used in the effective monodomain and phase field models include the four Landau parameters, $a_Q, b_Q, c_Q$, and $g$ and the Young’s modulus and Poisson ratio are denoted by $E$ and $\nu$, respectively.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Effective Monodomain</th>
<th>Phase Field Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_Q$</td>
<td>$-2.6 \times 10^8 \frac{\text{N-m}^6}{\text{C}^4}$</td>
<td>$-7.43 \times 10^9 \frac{\text{N-m}^6}{\text{C}^4}$</td>
</tr>
<tr>
<td>$g$</td>
<td>$5.0 \times 10^7 \frac{\text{N-m}^2}{\text{C}^4}$</td>
<td>$5.0 \times 10^{11} \frac{\text{N-m}^6}{\text{C}^4}$</td>
</tr>
<tr>
<td>$b_Q$</td>
<td>$-6.24 \times 10^9 \frac{\text{N-m}^{10}}{\text{C}^6}$</td>
<td>$-1.2 \times 10^{11} \frac{\text{N-m}^{10}}{\text{C}^6}$</td>
</tr>
<tr>
<td>$c_Q$</td>
<td>$2.08 \times 10^{10} \frac{\text{N-m}^{14}}{\text{C}^8}$</td>
<td>$6.9 \times 10^{11} \frac{\text{N-m}^{14}}{\text{C}^8}$</td>
</tr>
<tr>
<td>$E$</td>
<td>$8.0 \times 10^9 \text{ Pa}$</td>
<td>$8.0 \times 10^9 \text{ Pa}$</td>
</tr>
<tr>
<td>$\nu$</td>
<td>$0.35$</td>
<td>$0.35$</td>
</tr>
</tbody>
</table>

The free energy that is defined by $g = \psi - E_i P_i$ where $E_i$ is the electric field in the spatial configuration. A gradient based minimization is applied by satisfying, $\frac{\partial g}{\partial P_i} = 0$ for $i = 1, 2, \text{ and } 3$, at each electric field increment.

Using the effective monodomain parameters in Table 3, numerical simulations are conducted to first predict spontaneous strain, dielectric behavior, and piezoelectricity for different crystal orientations. The spontaneous strain predictions for an effective monodomain are $E_{s33}^* = 1\%$, $E_{s22}^* = E_{s11}^* = -0.34\%$ for a ferroelectric with polarization oriented in the $X_3$ direction. The spontaneous polarization for this case is $P_s^* = 0.58 \text{ C/m}^2$. The dielectric constant and piezoelectric behavior is quantified at different angles by rotating the local coordinates in the $X_2 - X_3$ plane for an applied field fixed in the $X_3$ direction. The slope of the applied field versus strain and polarization is obtained at different angles and is plotted in Figure 5. The orientation of the polarization is found to have a dramatic effect on the dielectric and piezoelectric response. The relative dielectric constant is largest when the polarization is orthogonal to the field and approaches a small, positive number when the field and polarization are aligned. The piezoelectric coefficient ($d_{333}$) is predicted to be slightly negative when the
Figure 5: Polar plot of the relative dielectric constant and piezoelectric coefficient \( d_{333} \) as a function of the polarization orientation. The model is rotated in the \( X_2 - X_3 \) plane. The maximum dielectric constant is 1676 and occurs at \( 0^\circ \) while the maximum piezoelectric coefficient is \( d_{333} = 1124 \) pm/V and occurs at \( \theta = 35^\circ \) based on the parameters in Table 3.

Polarization is aligned with the field \( (\theta = 90^\circ) \). As the angle is reduced from \( 90^\circ \) to \( 0^\circ \), the coefficient \( d_{333} \) increases until it reaches a maximum at \( \theta = 35^\circ \) and then approaches zero as the angle approaches zero. The results compare well with recent time-resolved x-ray experiments on tetragonal phase PZT (Jones et al., 2007; Pramanick et al., 2011). The predictions in the linear regime suggests polarization rotation is the primary source of deformation in poled ferroelectric materials. This is in contrast to most other models in the literature.

The linear piezoelectric predictions are compared with nonlinear ferroelectric switching to illustrate how the model predicts major loop polarization-electric field hysteresis and strain-electric field butterfly hysteresis. The same gradient based optimization scheme is applied for large bi-polar fields to predict polarization switching and deformation. The results for an initial angle between the field and polarization of \( \theta = 15^\circ \) is illustrated in Figure 6. The results show the conventional hysteresis response. Similar behavior is observed at other angles except the piezoelectric response and the coercive field varies as a function of the
crystal orientation relative to the field. Moreover, the relative dielectric susceptibility, defined in $P_i = \chi_{ij}^\epsilon \epsilon_0 E_j$ where $\epsilon_0$ is permittivity of free space, changes for different polarization orientations, but ranges from approximately $\chi_{33}^\epsilon = 50$ to 1000 similar to the perturbation analysis in Figure 5. This value is comparable to many ferroelectric materials and therefore the model reasonably predicts both dielectric and electromechanical behavior by only introducing four Landau coefficients, a Young’s modulus and a Poisson ratio. Note that the coercive field is strongly dependent on the anisotropic energy constant $g$ although this term does not directly contribute to the field-coupled Landau stress. This term penalizes 90° switching as illustrated previously in Figure 2(a) and therefore affects the field-induced polarization rotation and electric field coercivity to 90° polarization switching. As this coefficient increases, larger coercive energy barriers for 90° switching occur while simultaneously reducing the piezoelectric response.

These results are based on an idealized monodomain single crystal, whereas in realistic materials, many domains and grains influence the constitutive behavior. To account for a more realistic estimate of the material behavior, the free energy was implemented into the same finite element framework discussed in Section 4.2 for liquid crystal elastomers except the model used the ferroelectric Landau energy within a time-dependent Ginzburg-Landau equation. This equation is coupled with both linear momentum and Gauss’ law, $D_{i,i} = (\epsilon_0 E_i + P_i)_i = 0$ where $\epsilon_0$ is the permittivity of free space. Using this approach similar deformation from an initial polydomain state was observed during polarization rotation induced by an applied electric field. The results were obtained by poling a random polydomain model in two dimensions. The main distinction between the idealized monodomain and the phase field polydomain was the magnitude of the Landau parameters necessary to stabilize the domain structure due to the internal fields due to the introduction of Gauss’ law, unlike in the effective monodomain model. The Landau parameters were increased by two to three orders while holding the ratios approximately fixed so the spontaneous polarization was comparable to the idealized monodomain. This increase in the Landau parameters increased the spontaneous strain from 1% to approximately 10% as well as the coercive field as illustrated in Figure 6.
While the magnitude of spontaneous strain is larger than the typical experimental value for tetragonal phase ferroelectric materials, the effect of polarization rotation predicts positive strain increments until the model is fully poled. Once this occurs, the strain increments are slightly negative for any larger applied fields.

5 Discussion

An active material nonlinear continuum modeling framework has been developed to predict field-coupled nonlinear material behavior in a relatively broad range of active materials. Through the use of nonlinear continuum mechanics and rotational invariant order parameters, it was shown that scalar and vector order parameters induce hydrostatic spontaneous deformation at equilibrium. This somewhat surprising result for the vector order parameter shows that explicit coupling could be added into the material model to potentially improve the qualitative predictions of unusual active material coupling presented here. To further explore the effect of finite deformation and coupling with microstructure order parameters, the second order tensor order parameter $Q_{ij}$ was shown to induce anisotropic deformation for certain
ratios of the Landau coefficients. The magnitude and sign of the spontaneous deformation induced by \( Q_{ij} \) depended on three Landau parameters where decoupling was determined to occur for the ratio \( c_Q = \frac{-2b^2_{ij}}{a_Q} \). For values that were less than or greater than this ratio, either prolate or oblate spontaneous deformation was predicted and used to model liquid crystal elastomers and ferroelectric materials.

Specific attributes of the model were first validated on chemically deforming materials by introducing a chemical potential balance to accommodate changes in deformation as a function of chemical absorption from absorbing gases from the surrounding environment. This was coupled with nonlinear mechanics to obtain stresses induced by changes in water vapor concentration. A fourth order chemical potential parameter was implemented numerically to
predict deformation observed experimentally (Harris et al., 2005, 2007, 2006). As expected, changes in concentration lead to swelling; however, large anisotropic bending deformation was predicted when the model was coupled with an orthotropic elastic free energy function that represented the glassy elastomer network. It was shown that bending away from the water vapor source occurs due to a concentration gradient of water vapor through the thickness of the film. It should be noted that the chemically coupled stress given by (21) always predicts compressive stress which creates swelling under zero applied traction. Thus, the reference concentration $c_0$ is important in cases where shrinking may occur such as from changes in polarity or pH due to absorption of the chemicals in the environment. Order-disorder processes due to the underlying liquid crystal director may also contribute to deformation; however, the scalar concentration relation is found to provide reasonable predictions of concentration induced deformation.

The second numerical example illustrates how the nonlinear continuum model predicts soft elastic behavior or lack thereof in polydomain liquid crystal elastomers as a function of cross-linking in the isotropic or nematic state. Recent experiments have shown that under certain cross-linking conditions, polydomain specimens can exhibit soft elastic behavior similar to the well-known stress-strain plateau characteristics in monodomain liquid crystal elastomer specimens (Urayama et al., 2009). The polydomain structure at the onset of cross-linking had a significant impact on the nonlinear stress-strain constitutive behavior. For example, cross-linking in the nematic (lower temperature) state produced no soft elastic behavior. The soft elastic behavior was recently modeled using a set of homogenized free energy functions that depend on a residual deformation gradient; however, stress-strain behavior in the nematic cross-linked state was not considered in the model (Biggins et al., 2009). Here, changes in the soft elastic behavior are modeled as a function of cross-linking by introducing a set of Landau coefficients that decoupled or coupled spontaneous deformation with time-dependent microstructure evolution. The ratio of the Landau coefficients was found to have a dramatic effect on the soft elastic stress strain curve. For typical prolate deformation (positive deformation in the liquid crystal director orientation), soft elasticity was predicted for the isotropic
cross-linked state. In the nematic cross-linked state where no spontaneous deformation occurs, the stress-strain behavior is completely hyperelastic with no soft elasticity. The result provides a relatively simple methodology to predict significantly different constitutive behavior. However, note that quantitative model fits have not been done. This requires matching both changes in the order parameter and nonlinear deformation with the Landau coefficients. These issues will be explored in a future analysis.

In the third example, the nonlinear constitutive model was applied to ferroelectric materials where the anisotropic energy function $\psi_{\phi^1}$ was combined with the Landau-deGennes free energy function $\psi_Q$. This free energy function was chosen over vector order parameter free energy function $\psi_{\phi^2}$ since it allowed for predictions of anisotropic deformation without introducing explicit coupling between polarization and strain. As described in Section 3.4, the vector order parameter (i.e., polarization in this case) only induces hydrostatic stress and therefore would not produce any changes in deformation during polarization rotation. Alternative to introducing the tensor order parameter, explicit coupling could be added into the model to predict many of the observed coupling behavior in ferroelectric materials. It is important to note however that if explicit coupling is used, positive spontaneous strain in the direction of polarization will also lead to a positive $d_{333}$ coefficient when the external field is aligned with the polarization. Recent data (Pramanick et al., 2011) suggest negligible lattice strain for co-aligned fields and polarization where the majority of piezoelectricity is due to heterogeneous microstructure and polarization rotation. The proposed model that uses a second order tensor order parameter appears to fit this data more closely. This is somewhat surprising if the second order tensor order parameter is considered analogous to a linear quadrupole. This is because dipole energy is typically larger than the quadrupole energy (Loudon, 2000). A more rigorous analysis of the quadrupole tensor, its work conjugate electric field gradient, and potential deformation gradient coupling should be further explored to quantify these different effects on the electromechanical constitutive behavior.
6 Concluding Remarks

A nonlinear, field-coupled constitutive model has been developed and numerically implemented to correlate microstructure evolution with deformation from external mechanical loads, fields, and chemical absorption. The model illustrates when the effect of finite deformation coupling with microstructure becomes important or can be neglected when modeling microstructure induced deformation in active materials. By introducing a relatively small number of material parameters in the spatial domain, relatively complex nonlinear mechanics and microstructure evolution was predicted. This was achieved by transforming the spatial description of free energy and field quantities to the reference configuration. Reasonable correlation of complex liquid crystal elastomer nonlinear mechanics and chemically induced deformation was predicted. The model also predicted both anisotropic piezoelectricity and ferroelectric behavior using four Landau parameters and isotropic elastic coefficients. The ferroelectric results compared qualitatively with time-resolved x-ray experiments given in the literature which is different than the conventional tetragonal lattice distortion model for lead zirconate titanate.

7 Acknowledgment

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8 Appendix

8.1 Nominal Stress Relations

The nominal stress for the quadrupole tensor is obtained from

\[ s_{iK}^Q = \frac{\partial \tilde{\psi}_Q}{\partial F_{iK}} \]

and explicitly given by

\[ s_{iK}^Q = 2 \left( aJ^{-1} F_{iM} C_{NQ} \tilde{Q}_{KQ} \tilde{Q}_{MN} + cJ^{-2} F_{iM} C_{NQ} C_{RS} \tilde{Q}_{QR} \tilde{Q}_{MN} \tilde{Q}_{SK} \right) + \]

\[ \left( +dJ^{-3} F_{iM} C_{MQ} C_{RS} C_{TA} \tilde{Q}_{AK} \tilde{Q}_{ST} \tilde{Q}_{QR} \tilde{Q}_{MN} \right) \]

\[ -H_{iK} \left( \frac{a}{2} C_{MR} C_{NS} \tilde{Q}_{MN} \tilde{Q}_{RS} + \frac{2c}{3} C_{NR} C_{SA} C_{MB} \tilde{Q}_{MN} \tilde{Q}_{RS} \tilde{Q}_{AB} \right) \]

\[ \left( \frac{3d}{4} C_{NR} C_{SA} C_{BC} C_{DM} \tilde{Q}_{MN} \tilde{Q}_{RS} \tilde{Q}_{AB} \tilde{Q}_{CD} \right) \]

where \( C_{NQ} = F_{kN} F_{kQ} \). This result is based on the free energy given by (28) which leads to the Cauchy stress given by (30).

It was noted in Section 3.3 that the anisotropic free energy given in (22) does not contribute to the field-coupled stress. This free energy is written in the reference configuration as

\[ \tilde{\psi}_{\phi_1} = \frac{gJ^{-3}}{4} \left| (C_{MN} C_{PQ} - C_{MP} C_{NQ}) \tilde{\phi}_M \tilde{\phi}_N \tilde{\phi}_Q \tilde{\phi}_Q \right| \]

and the nominal stress associated with this free energy component is

\[ s_{iS}^{\phi_1} = \frac{gJ^{-3}}{2} \left| C_{MN} \tilde{\phi}_M \tilde{\phi}_N - C_{MN} \tilde{\phi}_M \tilde{\phi}_N \tilde{\phi}_A \tilde{\phi}_B \left( \frac{C_{AB}}{|C_{SQ}|} F_{rQ} - \frac{C_{AB}}{|C_{PS}|} F_{rP} \right) \]

using the identity \( \frac{\partial (C : C)^{1/2}}{\partial C} = \frac{C}{|C|} \). Obviously, the term in the absolute value brackets is zero.

References


